COMPUTATIONAL NANO-MORPHOLOGY: MODELING SHAPE AS WELL AS SIZE

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Abstract. Although great advances have been made in controlling the size of nanoparticles, variations of some properties still remain due to a dependence of the property not only on size, but also on the morphology. Therefore, nano-morphology must be carefully controlled to reliably synthesize nanoparticles with uniform properties. Here, a thermodynamic model designed to describe the shape of nanoparticle as a function of size and chemical environment will be outlined. It will be shown that the model may be used to explain how the shapes of nanoparticles differ from their macroscopic counterparts, and to predict the morphology of nanoparticles under desired conditions.

1. INTRODUCTION

As the demand for nanomaterials tailored to particular applications increases, so to the need for robust, monodispersed nanomaterials with reproducible and highly uniform properties will grow. It has been widely shown that many fundamental properties of nanomaterials have a strong dependence on particle size [1,2]; while other properties (such as quantum confinement [3]) have no macroscopic analogue. Although great advances have been made in controlling the size of nanoparticles, variations in some properties still remain due to a dependence on the nano–morphology.

More often now, nano–morphology is being found to be the critically important to the properties of many nanomaterials, such as nanocatalysis [4] and surface functionalization [5,6]. For example, it has been shown that organic molecules bind preferentially to certain surface sites, the position and number of which is explicitly linked to the nano–morphology [5,6]. Similarly, shape dependence in the optical and electronic properties quantum dots has been observed; such as quantum confinement [7] and luminescent properties [8,9], as well as the g-factors of semiconductor quantum dots [10] (Zeeman splitting of the ground state). Nanomagnetism has also been found to be shape dependent [11], and the morphological dependence of the characteristic switching fields of well-separated dots has been demonstrated by Novosad *et al.* [12].

In addition to the properties of isolated nanoparticles, the collective properties of nanoparticle arrays and other nano–architectures may also be dependent on shape. For example, the order and self–assembly of arrays of metallic nanoparticles has been found to be superior for uniformly faceted particles compared to spherical ones [13-15]. Therefore, in order to synthesize nanoparticles with uniform and reliable properties, the nano–morphology must be carefully controlled. In general the driving forces for variations in nano–morphology may be either thermodynamic or kinetic. More precisely,

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parameters such as size [16], temperature [17], chemical environment [18], electric fields [19], light [20,21], substrates [22,23], surfactants [24], and composition (dopants) [25] may be used to control nano-morphology.

Accurate explicit computational studies of nanoparticles, that account for factors in-fluencing the experimental parameters listed above, are very computationally demanding and difficult to extend to sizes above 1–2 nanometers. This is not just because of the large computational resources re-quired to calculate the optimized shape of (reason-ably sized) nanoparticles with first principles meth-ods, but also because of the large set of structures that must be explicitly examined in order to effec-tively sample structure–space. Even when order–*N* methods and massively parallel computer become readily accessible to all, the study of size *and shape* using traditional approaches will still be dependent upon comparing *Nn* structures, where *N* is the num-ber of size increments and *n* is the number of crys-tallographic directions in which the shape is varied.

It is therefore desirable to use an analytical ap-proach, based on a limited set of experimental or theoretical data. Previous analytical work pertain-ing to macro-scale crystal morphology [26] began with the classical work of Wulff [27] predicting the shape of macroscopic crystals based on the mini-mization of the total surface energy. Later, the ther-modynamic stability of faceted and 'rounded' shapes were revisited by Herring [28]. The total energy of different shapes as a sum of bulk and surface ener-gies and a uniform bulk strain were addressed by Cleveland and Landman [29], who predicted stable shapes of nickel in agreement with atomistic simu-lations; and Moll *et al*. [30] studied the influence of GaAs surface tension on the equilibrium shape of InAs quantum dots, using density functional calcu-lations of edge energies, surface energies and sur-face tensions combined with finite element calcula-tions of elastic energy. Most recently, Silly and Castell [31] reported a model for the shape of Pd nano-islands on $SrTiO_2$ surfaces, using shape pa-rameters defined in terms of ratios of (100) and (111) surface energies.

Outlined here is a thermodynamic model de-signed to describe the shape of nanoparticle as a function of size and chemical environment [32]; and an explanation of how to implement the model to investigate the dependence of nano-morphology on a number of experimentally relevant parameters.

2. MULTI-SCALE THERMODYNAMIC MODEL

The model describes the morphology of arbitrary (iso-lated) nanomaterials as a function of size, shape, temperature and chemical environment [32], based on an expansion of the Gibbs free energy. For a given nanoparticle of material in a phase *x*, the free energy may be expressed as a sum of contribu-tions from the particle bulk, surfaces, edges and corners, such that,

$$G_0^x = G_x^{bulk} + G_x^{surface} + G_x^{edge} + G_x^{corner}. \tag{1}$$

where,

$$G_x^{bulk} = \Delta_f G_x^0(T),$$

$$G_x^{ende} = \frac{M}{\rho_x} p \sum_j g_j \lambda_{xj}(T),$$

$$G_x^{surface} = \frac{M}{\rho_x} q \sum_i f_i \gamma_{xi}(T), \tag{2}$$

$$G_x^{corner} = \frac{M}{\rho_x} w \sum_k h_k \varepsilon_{xk}(T),$$

in terms of the molar mass *M* and density ρ_x of the material in a phase *x*. Here (in terms of the tem-perature *T*), $G_x^{surface}$ is expressed in terms of the sur-face to volume ratio *q* and $\gamma_{xi}(T)$ the surface free energy of facet *i*; G_x^{edge} is expressed in terms of the edge to volume ratio *p* and $\lambda_{xj}(T)$ the edge free en-ergy of edges *j*; and G_x^{corner} is expressed in terms of the corner to volume ratio *w* and $\varepsilon_{xk}(T)$ the corner free energy of corners *k*. The weighting factors are defined so that,

$$\sum_i f_i = \sum_j g_i = \sum_k h_k = 1. \tag{3}$$

The values of $\gamma_{xi}(T)$, $\lambda_{xj}(T)$ and $\varepsilon_{xk}(T)$ must be cal-culated for all *i, j* and *k* of interest, using (the same) appropriate computational method (such as density functional theory), and to the same convergence; and the ratios *q, p* and *w* and the weighting factors must be calculated explicitly for each shape and the facets therein.

However, this does not account for the effects of surface tension on the particle, which are signifi-cant at the nanoscale and may not be ignored. The surface tension produces an effective pressure on the particle, which may be addressed by introduc-ing the resulting (usually compressive) volume dila-tion *e*. The effect of this dilation will be to reduce the

molar volume. Therefore the model, including the effective pressure becomes:

$$G_x^0 = \Delta_f G_x^0(T) + \frac{M}{\rho_x}(1 - e)$$

$$\left[q\sum_i f_i \gamma_{xi}(T) + p\sum_j g_j \lambda_{xj}(T) + w\sum_k h_k \varepsilon_{xk}(T) \right]. \quad (4)$$

In general, the volume dilation due to the surface tension σ (and the material compressibility β) may be approximated using such expressions as the Laplace-Young equation, where *R* is the mean radius of the particle, so that,

$$e = \frac{2\beta\sigma_x(T)}{R}, \quad (5)$$

where,

$$\sigma_x(T) = \sum_i f_i \sigma_{xi}(T). \quad (6)$$

This approach assumes that the particles are spherical, and that the surface tension is independent of orientation. The pressure induced at any point of the surface is directed to the center of curvature and is proportional to the curvature at that point. This approximation has been previously compared with a more general expression derived by Stoneham [33] for facetted crystals, and shown to give a good description of faceted nanoparticles over ~500 atoms [32], however alternative methods of for calculating *e* may just as easily be used.

2.1. Range of applicability

In practices the calculation of all *j* edges and *k* corners can prove as computationally intensive as explicitly calculating the optimized geometry of complete, isolated particles. Also the importance of λ_{xj} and ε_{xk} in the total free energy of the system is largely unknown. Using geometric arguments (and energetic analogies), it has been previously demonstrated that the contribution from the edges and corners is expected to be considerably smaller than that of the surfaces of nanocrystals larger than ~ 3 nm, and can be altogether neglected over ~ 5–6 nm. Therefore, at small nanoparticles less than 3 nm it is still preferable to examine each morphology explicitly by undertaking suitable calculations of isolated nanoparticles (using *ab initio* or tight–binding methods).

Similarly, at large sizes, in the range of 75–100 nm in diameter, the free energy of the surfaces is less than 10^{-4} J/mol, making the energetics of the surface less significant, and other bulk effects more significant. In this size regime, for example, the macroscopic (bulk) strain is as important as the surface strain, and the bulk entropy will be as important as the surface entropy. The present model does include the bulk strain, but does not explicitly include other macroscopic thermodynamic arguments.

For these reasons, this model is best applied to particles in the range 3–100 nm.

2.2. Model dependenices on experimentally relevant parameters

Excluding the edge and corner effects and applying the model only to particles in the range approximately 3–100 nm, leaves the surface contribution. In general, the size dependence is introduced primarily by the surface to volume ratio *q*, whereas the shape dependence is introduced by *q* (which is different for a cube, for example, and an octahedron) and the weighted sums of the surface energies and surface tensions corresponding to the surfaces present in the particular morphology under consideration. The most basic application of the model it therefore to compare the stability of various morphologies of a given material, as a function of size.

It is also apparent, that through the calculation of the surface energies and surface tensions a number of other dependencies may be introduced; the most obvious of which is temperature dependence (as indicated by Eqs. (4) and (5)). Often the energetics of surfaces are determined in the presence of adsorbates, usually as a function of the adsorbate chemical potential. By determining the surface energies (and tension) as a function of chemical potential, or making explicit calculation of these quantities with type and coverage of adsorbates (for each of the surfaces *i* under consideration) it is possible to compare the shape of nanoparticles with different surface chemistry [35]. Further, by calculating the surface energy (and tension) of various reconstructions, the dependence of nano–morphology on different surface structures may also be investigated, even in the presence of defects.

Perhaps the most useful aspect of this model is the opportunity to optimizes the shape of nanoparticles with respect to any of these parameters, to determine the equilibrium nano-morphology under prescribed conditions.

2.3. Optimizing nano-morphology

The standard method for determining the equilibrium morphology of a material is to generate the Wulff construction [27] using only the surface free energies. The Wulff construction describes the equilibrium shape of crystals, given by the convex envelope of planes (perpendicular to the surface normals) that minimizes surface energy for a given enclosed volume. Equivalently, the distance of a surface plane from the center-of-mass of the crystal is proportional to the surface energy of that plane. The Wulff construction accurately describes the shape of crystals at the macroscale, but does not account for surface tension (which is significant at the nanoscale), nor the desire of nanocrystals to minimize the *total surface to volume ratio*. Therefore it is possible that the morphologies of nanocrystals may deviate from the macroscopic Wulff shape.

Using the model outlined here it is possible to compare any shape of nanoparticle (as a function of temperature, size and chemical environment) by programming in desired morphologies; however (as mentioned above) it is also possible to define the shape using independent spacial variables, and optimize the shape as a function of any particular dependency.

Take for example, the shape–continuum formed when changing from a cube to an octahedron (through truncated cube, cuboctahedron, and truncated octahedron) via successive truncation of the cube corners. By defining the shape (specifically, the volume and surface area of the various facets) in terms of geometrically independent parameters such as the side length of a cubic facet (**A**) and the degree of truncation in the octahedral direction (**B**), the total Gibbs free energy (corresponding to a certain size, temperature and surface chemistry), may be minimized with respect to the ratio **B/A**. This type of morphological optimization may be readily performed using a numerical minimization technique such as a conjugate gradient scheme.

3. CONCLUSION

For a number of nanomaterials, the thermodynamic model described above has been shown to have excellent predictive and explanatory capabilities. It has been used to examine the equilibrium morphology of nanocrystalline diamond [32], silicon [32], germanium [32], titanium nitride [34] and titanium dioxide [35-37]. In each case, the results are in excellent agreement with experiment.

Since this model can be used for any type of material, any crystallographic system it can be used to predict phase transitions as a function of shape and size by equating free energies for the most stable shapes of opposing phases. For example, by calculating G_x^o of the anatase and rutile TiO_2 polymorphs, the size and shape dependence of the anatase–to–rutile phase transition has been investigated [36] under various chemical conditions[35, 37].

Planned improvements to the model include the addition of terms to describe defects such as twinning, particle–particle and particle–substrate interfaces. It is anticipated that this model will become a valuable tool for the computational study of nano–morphology in the future.

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